Large room-temperature magnetocaloric effects in $Fe_{0.8}Mn_{1.5}As$

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In $Fe_{0.8}Mn_{1.5}As$ compound, an external magnetic field induces a metamagnetic transition from an antiferromagnetic phase to a ferrimagnetic phase above $T_s=285$ K, leading to large magnetocaloric effects around room temperature. Instead of showing inverse magnetocaloric effects, the sign of the entropy change ΔS_M in the compound is unexpectedly negative, revealing a different mechanism. The maximum value of ΔS_M is 6.2 J/kg K at 287.5 K for a magnetic field change of 5 T. The study on systems with antiferromagnetism-related metamagnetic transitions may open an important field in searching good materials for room-temperature magnetic refrigeration. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2784170]

Currently there is a great deal of interests in utilizing the magnetocaloric effect (MCE) as an alternate technology for refrigeration replacing the common gas compression/expansion technology.[1–3] Much attention in particular has been paid to room-temperature magnetic refrigeration.[4–11] Consequently it is of great importance to explore new compounds which exhibit large entropy changes near room temperature. In general, investigation for MCE has been focused on ferromagnets, such as $Gd_5(Ge_{1-x}Si_x)_4$,[12] $MnFeP_{0.45}As_{0.55}$,[4] $MnAs_{1-x}Sb_x$,[5] and $La(Fe_{1-x}Si_x)_{13}$ and its hydrides,[13,14] for large magnetic entropy changes ΔS_M can happen in the vicinity of magnetic-phase transitions from paramagnetism to ferromagnetism (FM). On the other hand, many antiferromagnetic (AF) systems show temperature/field-induced AF/FM,[15–17] AF-collinear/AF-triangular,[18,19] or AF ferrimagnetic (FI) transitions[20] involving large entropy changes. It is worthwhile noting that the sign of entropy change in these AF systems is positive, and this behavior is known as inverse MCE. Here we report a large room-temperature MCE originated from a field-induced metamagnetic transition (AF/FI) in $Fe_{0.8}Mn_{1.5}As$ compound. In sharp contrast with the AF systems stated above, instead of showing inverse MCE, the sign of entropy change ΔS_M in the compound is unexpectedly negative, revealing a different mechanism.

The first-order AF to FI transition on cooling has been reported for the system $Fe_{a-x}Mn_xAs$ $(1.95 \leqslant a \leqslant 2.35)$.[21–23] The transition metals in these compounds occupy two different sites, i.e., site 1 and site 2, and the magnetic structure can be regarded as a stacking of triple layers of site 2–site 1–site 2. It is believed that the AF state at high temperatures has a spin structure of Mn_2As type, while the FI spin structure at low temperatures is of Mn_2Sb type.[21,24] The moments of all triple layers are parallel in the FI state, while the arrangement between spins becomes antiparallel in the AF state.[25–27]

Polycrystalline $Fe_{0.8}Mn_{1.5}As$ compound was synthesized by a method described elsewhere.[27] X-ray diffraction was carried out to verify that the sample yielded diffraction peaks characteristic of a single phase with Cu_2Sb-type tetragonal structure. The magnetic properties were measured using a superconducting quantum interference device magnetometer at applied magnetic fields up to 5 T at temperatures from 5 to 350 K. The change of the magnetic entropy was calculated from the *M-H* plots at various temperatures close to 285 K, with a temperature step of 5 K.

The temperature dependence of the magnetization for the $Fe_{0.8}Mn_{1.5}As$ compound was measured in the zero-field cooled process. The sample was cooled from room temperature to 5 K without application of an external magnetic field, and then the magnetization as a function of temperature was recorded in a field of 0.01 T during the warming process from 5 to 350 K (shown in Fig. 1). It can be clearly seen that

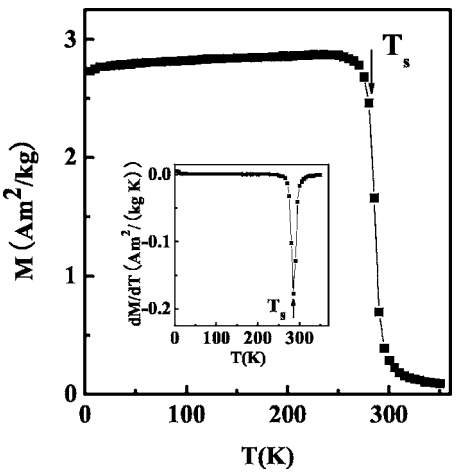

FIG. 1. Temperature dependence of the magnetization of $Fe_{0.8}Mn_{1.5}As$ at 0.01 T. The inset shows the first order derivative of the magnetization (dM/dT) as a function of temperature.

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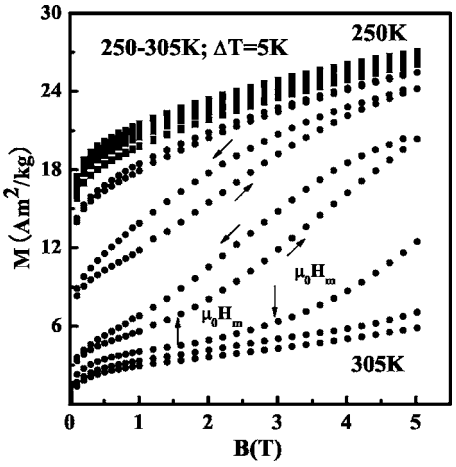

FIG. 2. Field dependence of the magnetization of $Fe_{0.8}Mn_{1.5}As$ at the temperatures indicated.

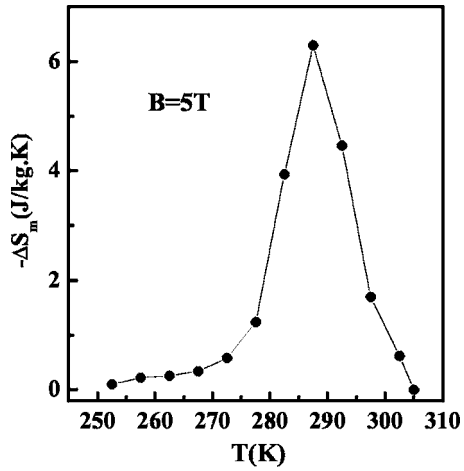

FIG. 3. Magnetic entropy changes of $Fe_{0.8}Mn_{1.5}As$ in an external field change of 5 T.

with increasing temperature, the magnetization drops abruptly at a phase transition temperature T_s of about 285 K, showing a first-order magnetic phase transition from the FI to the AF state. As shown in the inset of Fig. 1, this transition temperature was defined as the corresponding minimum temperature in the plot of the first order derivative of the magnetization (dM/dT) as a function of temperature. To explore the influence of external fields on the FI-AF transition, the $M(H)$ curves are shown in Fig. 2. At 280 K, the magnetization rose abruptly at a rather low field and rapidly showed a tendency to saturate, suggesting that the compound was in FI state at this temperature. In sharp contrast, at 290 and 295 K, after an initially linear increase at low fields, revealing that the compound was in an AF state at zero field, the magnetization increased abruptly at critical fields $\mu_0 H_M$ of about 1.6 and 3 T, respectively. This abrupt increase of the magnetization indicates a field-induced AF-FI transition. Meanwhile, clear hysteretic behaviors appeared in the magnetization versus magnetic fields curves for 290 and 285 K. An abrupt rise in magnetization accompanied by a clear hysteretic behavior is traditionally taken as evidencing a first order magnetic phase transition. At 305 K, the magnetization maintained a linear increase with increasing the field: a typical AF behavior.

As a large MCE often appears at the magnetic transition, a large magnetic-field-induced ΔS_M is expected in $Fe_{0.8}Mn_{1.5}As$ from the magnetization curves in Fig. 2. The value of the isothermal $\Delta S_M(T,H)$ is given by the following expression associated with the Maxwell relationship:

$$\Delta S_M(T,H) = S(T,H) - S(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \qquad (1)$$

The sign of ΔS_M is determined by the sign of $\partial M/\partial T$, as shown in formula (1). Figure 3 gives $\Delta S_M(T)$ curves of $Fe_{0.8}Mn_{1.5}As$ compound with a magnetic field change of 5 T. Here the sign of ΔS_M is negative. That is, the present compound shows a conventional MCE cooling by adiabatic demagnetization. Considering that almost all the antiferromagnetism-related metamagnetic transitions show inverse MCE,[15–20] the MCE in $Fe_{0.8}Mn_{1.5}As$ is quite unusual and unexpected. As opposed to those AF systems showing inverse MCE, the spin arrangement in the present compound is FI in low temperatures and AF in high temperatures. In addition, as shown in Fig. 2, the critical fields increase with the increase of temperature. This behavior is quite different from the critical field behaviors observed in the AF systems with inverse MCE, where critical fields decrease with increasing temperature. So it is understandable that the sign of the entropy change (ΔS_M) in $Fe_{0.8}Mn_{1.5}As$ is negative. Some authors tried to explain the field-induced inverse MCE.[15–20] They pointed out that as opposed to cooling by adiabatic demagnetization, cooling by adiabatic magnetization (inverse MCE) required an increase in configurational entropy on applying a magnetic field. Near the transition temperature, there occurred a magnetically inhomogeneous state. Due to the presence of mixed magnetic exchange interactions, the application of an external magnetic field led to further spin disorder in those systems, which made the configurational entropy increase.[28] It seems that this explanation is not suitable for the MCE in $Fe_{0.8}Mn_{1.5}As$. In the present compound, it is believed that the FI state in low temperatures is more order than the AF state in high temperatures. Consequently, an external field induces a metamagnetic transition from AF to FI and increases the extent of order of the total spin system, thus decreasing the magnetic entropy. The maximum ΔS_M with a field change of 5 T is 6.2 J/kg K at 287.5 K, meaning that the field-induced metamagnetic transition is responsible for the large ΔS_M in $Fe_{0.8}Mn_{1.5}As$. A larger ΔS_M near room temperature can be expected in the $Fe_{a-x}Mn_xAs$ ($1.95 \leqslant a \leqslant 2.35$) system by increasing the saturation magnetization through increasing the Fe/Mn ratio or replacing As with P or Sb. Furthermore, the transition temperature T_s in the present FeMnAs system can be set at any temperature from 153 to 345 K by a proper combination of metal/arsenic ratio $a(1.95 \leqslant a \leqslant 2.35)$ and Mn/Fe ratio.[21–23] This is practically meaningful because one can tune the maximum MCE in this temperature range without losing the large MCE. This temperature range is even wider than those in the well-known excellent candidates for magnetic refrigerants, such as $MnFeP_{1-x}As_x$ system,[4] in which the Curie temperature can be tuned between 168 and 332 K by varying the P/As ratio between 1.5 and 0.5. In the systems showing antiferromagnetism-related metamagnetic transitions, such as $Fe_{0.49}Rh_{0.51}$ (AF/FM),[15] Mn_3GaC (AF/FM),[16] ε-$(Mn_{0.83}Fe_{0.17})_{3.25}Ge$ (AF-collinear/AF-triangular),[19] and $Mn_{1.95}Cr_{0.05}Sb$ (AF/FI),[18] the first-order phase transition temperature is too low to make them good candidates for room-

temperature magnetic refrigeration except $Fe_{0.49}Rh_{0.51}$. However, the MCE in $Fe_{0.49}Rh_{0.51}$ is irreversible in alternating magnetic fields (i.e., it disappears after 1 cycle).[12] In the present system, cycling of a magnetic field does not induce an irreversible change in the magnetic and magnetocaloric behaviors. Lower cost for raw materials, compared with Gd, $Gd_5(Ge_{1-x}Si_x)_4$,[12] and NiMnGa (Ref. 29) alloys, is another advantage of the present system. Consequently, it is believed that the $Fe_{a-x}Mn_xAs$ ($1.95 \leqslant a \leqslant 2.35$) alloys are good candidates for room-temperature magnetic refrigeration.

In conclusion, with increasing temperature, tetragonal $Fe_{0.8}Mn_{1.5}As$ compound exhibits a first-order phase transition at $T_s = 285$ K from a FI phase to an AF phase and a large room-temperature MCE has been observed near the magnetic transition temperature. The maximum value of ΔS_M is 6.2 J/kg K at 287.5 K in a magnetic field change of 5 T and the sign of ΔS_M is unexpectedly negative, revealing a different mechanism. The study on systems showing field-induced metamagnetic transitions in relation to AF, as shown in $Fe_{0.8}Mn_{1.5}As$, may open an important field in searching good candidates for room-temperature magnetic refrigeration.

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